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(57) Abstract

Freeze-thaw stable water-in-oil emulsions include: an external phase comprising a polyalphaolefin fluid; an internal aqueous phase which contains a polyglyveryl fatty acid diester type non-ionic emulsifier having a HLB value of less than about 5, a non-ionic emulsifier having a HLB value of above about 8 and, optionally, an ethoxylated vegetable oil type non-ionic emulsifier having a HLB value of less than about 5, and an emulsion stabilizer.

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STABLE WATER-IN-SYNTHETIC HYDROCARBON FLUID EMULSIONS

This invention relates generally to water-in-oil type emulsions and more particularly to stable, high water content, water-in-oil type emulsions having alpha-olefin oligomer fluids such as polydecene fluids as the continuous phase, which can be formed at ambient temperatures.

Alpha-olefin oligomer fluids, often referred to in the art as "polyalphaolefins", have been used to replace mineral oils in a number of applications including personal care products such as lotions and creams. Cosmetic products containing polyalphaolefin fluids are described, for example, in published Japanese patent applications SHO (1977) - 72832 and SHO (1978) - 27772.

High water content water-in-oil emulsions are desirable from the standpoint of cost, less oily feel, and an enhanced cooling effect ("freshness") due to evaporation of the larger amount of water. A problem associated with high water content, water-in-oil emulsions made from alpha-olefin oligomer fluids, such as the commercially available polydecenes, is emulsion stability, especially when the products are subjected to several freeze-thaw cycles.

Freeze-thaw stable, long shelf life water-in-oil emulsions using alpha-olefin oligomer fluids have now been provided by using certain combinations of non-ionic emulsifiers. The emulsions can be formed at ambient temperatures, which saves energy.

In accordance with this invention there is provided a freeze-thaw stable water-in-oil emulsion composition comprising:

an external phase comprising a polyalphaolefin fluid;

an internal aqueous phase;

a non-ionic emulsifier system consisting essentially of a polyglyceryl fatty acid diester type non-ionic emulsifier having a HLB value of less than about 5, a non-ionic emulsifier having a HLB value of from about 8 to 10 and, optionally, an ethoxylated vegetable oil non-ionic emulsifier having a HLB value of less than about 5; and

an emulsion stabilizer.

Polyalphaolefin fluids are hydrogenated, branched chain liquids which are prepared by oligomerizing alpha-olefins which have from about 6 to 20 and, preferably, 8 to 14 carbon atoms. Preferred polyalphaolefins for use in the emulsion compositions of the invention have kinematic viscosities at 100°C of from about 2 to 20 cSt and especially preferred are polydecenes having viscosities of from about 2 to 12 cSt. These fluids constitute the external or continuous phase and in cosmetic applications act as an emollient. The fluids are, preferably, present in amounts of from about 5 to 40 and, more preferably, from about 9 to 25 weight percent of the emulsion compositions. The water is preferably present in the range of from about 50 to 85

weight percent of the emulsion compositions and more preferably from about 65 to 75 weight percent.

The non-ionic emulsifier system includes a polyglyceryl fatty acid diester type non-ionic emulsifier which has a HLB value of less than about 5.0 and preferably from about 4.0 to 4.9. Non-limiting examples include triglyceryl dioleate, diglyceryl dipalmitate and the like. Preferred are branched alkyl chain esters such as triglyceryldiisostearate. The emulsifier system also includes a non-ionic emulsifier which has a HLB value of from about 8 to 10. Preferred are polyoxyethylene sorbitan esters of fatty acids such as PEG (40) sorbitol septaoleate. The system can also include an ethoxylated vegetable oil type non-ionic emulsifier which has a HLB value of less than about 5 and preferably from about 4.0 to 4.9 such as PEG-7 hydrogenated castor oil.

The amounts of the emulsifier components are chosen to provide a combined HLB value of from about 5 to 7 depending upon the emulsifier system used and, preferably in a two-component system, about 5.9 for polydecenes, which value has been found to provide freeze-thaw and storage stable polydecene containing water-in-oil emulsions. The combined HLB value is a straight line relationship which can be readily calculated by multiplying the proportion of each emulsifier in the system by its HLB value and adding up the resulting values, as is known in the art. Although emulsifiers having HLB values above 10 will provide the required HLB value for the system, They do not provide stable emulsions. Likewise, the use of a vegetable oil

type emulsifier in a two component emulsifier system does not provide a stable emulsion. In general, the total amount of emulsifiers in the emulsion compositions will range from about 2 to 10 weight percent and, preferably, from about 4 to 7 weight percent.

The emulsions also contain from about 0.1 to 0.5 weight percent an emulsion stabilizer. Preferred are inorganic acid salts. Non-limiting examples of such inorganic salts include alkali metal salts, alkaline earth metal salts and aluminum salts of inorganic acids such as hydrochloric acid, sulfuric acid and nitric acid. Preferred inorganic salts include potassium sulfate, magnesium sulfate, potassium chloride, magnesium chloride and aluminum chloride. Other types of stabilizers, such as fatty acid salts could be used.

The emulsions can be used in a variety of applications such as drilling fluids and health care products such as pharmaceutical and cosmetic creams and lotions. The health care product emulsions will include one or more appropriate ingredients selected from emollients, preservatives, humectants, fragrances, thickeners, moisturizers, antifoam agents, opacifiers, colorants, covering agents, and active agents such as pharmaceuticals (antibiotics, antiseptics, antifungals, antihistamines, analgesics, etc.) vitamins, sunscreens, insect repellents, deodorants, antiperspirants, cleaning agents, moisturizers, and the like. Normally the total amount of these additive ingredients will not exceed about 10 wt. percent of the total emulsion composition.

The emulsions can be made by mechanical mixing techniques as known in the art at ambient temperatures, e.g. about 20 to 30°C.

The invention is further illustrated by, but is not intended to be limited to, the following examples wherein parts are parts-by-weight unless otherwise indicated.

Example 1

A stable water-in-oil emulsion is prepared at room temperature using the following ingredients:

Ingredient	Function	Amount
Part A		
PEG-7 Hydrogenated Castor Oil (HLB 4.7)	Emulsifier	1.7
Triglyceryl-3-Diisostearate) (HLB 4.7	Emulsifier	2.7
POE (40)-Sorbitol Septaoleate (HLB 9.5)	Emulsifier	2.5
Vitamin E	Vitamin	5.0
Polydecene (4 cSt at 100°C)	Emollient	16.6
Part B		
Glycerin	Humectant	3.0
Magnesium Sulfate	Stabilizer	0.3
Water	Diluent	67.2

Part C

Propylene Glycol & Diazolidinyl Urea & Methylparaben & Polyparaben	Preservative	1.0

The emulsifier system has a HLB value of about 6.4. The emulsion is prepared by adding Part B to Part A with mixing at 25-30°C until a uniform mixture is obtained (about 1 hour). Part C is then added with mixing to provide a lotion. The emulsion is stable through three freeze-thaw cycles and oven aging of 45°C for over one month. The vitamin E helps to provide a stable emulsion.

Example 2

A stable water-in-oil emulsion is prepared at room temperature using the following formulation.

Ingredient	Function	Amount
Part A		
Triglyceryl-3-Diisostearate	Emulsifier	5.2
POE (40) - Sorbitol Septaoleate	Emulsifier	1.7
Polydecene (4 cSt at 100°C)	Emollient	21.6
Part B		
Glycerin	Humectant	3.0
Magnesium Sulfate	Stabilizer	0.3
Water	Diluent	68.2

The emulsifier system (6.9 weight percent surfactants) has a HLB of about 5.9. The emulsion is prepared by adding Part B to Part A with mixing at room temperature (25 to 30°C) until a uniform mixture is obtained. The mixture is then homogenized for three minutes. The water-in-oil emulsion is stable through three freeze thaw cycles and oven aging for one month.

Example 3

A stable water-in-oil emulsion is prepared at room temperature using the following formulation:

Ingredient	Amount
Part A	
PEG-7 hydrogenated Castor oil	1.95
Triglyceryl diisostearate	3.25
POE (40)-sorbitol septaoleate	1.7
Polydecene (2 cSt at 100°C)	21.6
Part B	
Glycerin	3.0
$MgSO_4$	0.3
Water	68.2

Example 4

Stable water-in-oil emulsions are formed using the same ingredients and process as in Example 2 except that 3.8 parts of triglyceryl-3-diisostearate, 1.2 part of

POE (40)-sorbitol septaoleate and 23.5 parts of polydecene (5.0 weight percent surfactants) are used.

Example 5

Stable water-in-oil emulsions are formed using the same ingredients and process as in Example 2 except that 3.0 parts of triglyceryl-3-diisostearate, 1.0 part of POE (40)-sorbitol septaoleate, and 24.5 parts polydecene (4.0 weight percent surfactants) are used.

The advantages of the above emulsions include:

(1) Stability - these emulsions are stable after three freeze-thaw cycles and oven aging at 45°C for over one month.

(2) Silky Feel - the polydecene-containing lotion gives silkier, less greasy feel than mineral oil-containing ones.

(3) Energy Saving - Since these emulsions were prepared at room temperature it saves energy to prepare them.

(4) Low Cost - These emulsions can employ a large internal aqueous phase and still be freeze-thaw stable.

Comparison 1

A water-in-oil emulsion is prepared using the formulation as in Example 2, except that 5.2 parts of triglyceryl-3-diisostearate is replaced by 5.2 parts of PEG-7 hydrogenated castor oil. The resulting emulsion is not stable.

Comparison 2

A water-in-oil emulsion is prepared as in Example 2 except that the emulsifier system (6.9 weight percent surfactants HLB 5.9) is 6.1 parts of Span 60 sorbitan mono-ester or stearic acid (HLB 4.7) and 0.8 parts of Tween 60 POE derivative of sorbitan mono-ester of stearic acid (HLB 14.9). The emulsion is not stable.

Comparison 3

A water-in-oil emulsion is prepared as in Example 2 except that emulsifier system (6.9 weight percent surfactants HLB 5.9) is 5.98 parts of Brij 72 stearyl alcohol ethoxylate (HLB 4.9) and 0.92 part of Brig 76 stearyl alcohol ethoxylate (HLB 12.4). The emulsion is not stable.

What Is Claimed Is:

1. A freeze-thaw stable water-in-oil emulsion composition comprising:

an external phase comprising a polyalphaolefin fluid;

an internal aqueous phase;

a non-ionic emulsifier system consisting essentially of a polyglyceryl fatty acid diester type non-ionic emulsifier having a HLB value of less than about 5, a non-ionic emulsifier having a HLB value of from about 8 to 10 and, optionally, an ethoxylated vegetable oil type non-ionic emulsifier having a HLB value of less than about 5; and

an emulsion stabilizer.

2. The composition of claim 1 wherein said poly-alphaolefin fluid is derived from an α-olefin monomer having from 8 to 14 carbon atoms and has a kinematic viscosity of from about 2 to 12 cSt at 100°.

3. The composition of claim 2 wherein said poly- alphaolefin fluid is polydecene.

4. The composition of claim 3 wherein said emulsifier system has a HLB value of from about 5 to 7, and said emulsion stabilizer is magnesium sulfate.

5. The composition of claim 1 which includes at least one agent selected from the group consisting of fragrances, pharmaceutical compounds, sunscreens, insect repellents, vitamins, antiperspirants, cleaning agents, moisturizers, and deodorants.

6. The composition of claim 1 wherein said emulsifier system consists essentially of a polyglyceryl fatty acid diester type non-ionic emulsifier having a HLB value less than about 5 and a non-ionic emulsifier having a HBL of from about 8 to 10.

7. The composition of claim 6 wherein the polyalphaolefin fluid is polydecene and the HLB value of the emulsifier system is about 5.9.

8. The composition of claim 1 wherein the amount of polyalphaolefin fluid is from about 5 to 40 weight percent of the emulsion composition and the amount of water is from about 50 to 85 weight percent of the emulsion composition.

9. The composition of claim 1 which includes said ethoxylated vegetable oil type non-ionic emulsifier.

10. A freeze-thaw stable water-in-oil emulsion composition comprising:

an external phase which comprises a polydecene fluid having a kinetic viscosity of from about 2 to 4 cSt at 100°C, said fluid making up from about 9 to 25 weight percent of said composition;

an external aqueous phase the water in said aqueous pahse making up from about 65 to 75 weight percent of said composition;

a non-ionic emulsifier system consisting essentially of triglyceryl diisostearate and POE (40) - Sorbitol septaoleate in proportions to provide a combined HLB value of about 5.9; and

magnesium sulfate.

11. A freeze-thaw stable water-in-oil emulsion composition comprising:

an external phase which comprises a polydecene fluid having a kinetic viscosity of from about 2 to 4 cSt at 100°C, said fluid making up from about 9 to 25 weight percent of said composition;

an external aqueous phase the water in said aqueous phase making up from about 65 to 75 weight percent of said composition;

a non-ionic emulsifier system consisting essentially of triglyceryl diisostearate, POE (40) - Sorbitol septaoleate, and PEG-7 hydrogenated castor oil in proportions to provide a combined HLB value of about 6.4;

vitamin E; and

magnesium sulfate.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/50 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 15 no. 392 (C-0873) ,4 October 1991 & JP,A,03 161417 (KANEBO LTD) see abstract ---	1
A	EP,A,0 422 862 (RICHARDSON-VICKS INC.) 17 April 1991 see the whole document ---	1
A	WO,A,94 27574 (L'OREAL) 8 December 1994 see the whole document ---	1
A	EP,A,0 336 900 (WARNER-LAMBERT COMPANY) 11 October 1989 see the whole document ---	1

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	DATABASE WPI Week 9213 Derwent Publications Ltd., London, GB; AN 92-101987 & JP,A,04 045 842 (MITSUBISHI HEAVY IND KK) , 14 February 1992 see abstract ---	1
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Information on patent family members

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